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(54) CATALYST, METHOD OF MANUFACTURE AND USE THEREOF

(71) We, UOP INC., formerly Universal Oil Products Company, a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is generally well known that cracking involves the thermal decomposition, with or without the aid of a catalyst, of petroleum or heavy petroleum fractions to yield lower boiling more useful petroleum products. When said cracking is effected under an imposed hydrogen pressure, the process is referred to as hydrocracking and the resulting lower boiling petroleum fractions are substantially more saturated than would otherwise be the case. Hydrocracking is particularly useful to convert those higher boiling petroleum fractions boiling in the middle distillate range, or higher, to substantial yields of lower boiling more useful petroleum fractions. Thus, higher boiling petroleum fractions including those in the kerosine and gas oil boiling range, lubricating and white oil stocks, higher boiling materials such as fractionator bottoms from a conventional cracking operation, are converted to more useful lower boiling products usually comprising hydrocarbons in the gasoline boiling range.

Although hydrocracking can be accomplished thermally, improved conversion is realized utilizing a catalyst — typically a composite comprising a hydrogenation component and a cracking component. A catalyst's ability to convert the petroleum or heavy petroleum fraction to lower boiling products at a given severity level, e.g. temperature, pressure, etc., is generally referred to as activity, and selectivity refers to a

catalyst's ability to convert the petroleum or heavy petroleum fraction not only to lower boiling products but to specific lower boiling products such as a gasoline boiling range petroleum fraction. While the catalyst composition of this invention exhibits high activity and selectivity, it is particularly notable for its stability. Stability as herein contemplated relates to the rate of change in activity and selectivity with time, a lower rate denoting high stability. In practice, hydrocracking is effected at conditions to produce a constant yield of a given product, e.g. a petroleum fraction in the gasoline boiling range, with the severity level being periodically adjusted to attain this objective. The severity level is usually adjusted by increasing reactor temperature so that in fact the rate of change in the reactor temperature is indicative of catalyst stability.

The present invention seeks to provide a novel catalyst composition particularly useful as a hydrocracking catalyst of improved stability.

According to the present invention there is provided a catalyst composition comprising a hydrogenation component supported on a crystalline aluminosilicate composited with alumina, the composite being substantially free from amorphous silica and containing less than 4 wt.% alkali metal, and the hydrogenation component comprising a Group VIII metal component and a Group VIB metal component in a weight ratio (calculated as the metals) of from 1.5:1 to 9:1.

The invention also includes a process for the catalytic hydrocracking of a petroleum or heavy petroleum fraction in which a catalyst composition according to the invention is used as the catalyst.

The crystalline aluminosilicate-alumina composite on which the hydrogenation component is supported may be formed in any conventional or otherwise convenient man-

ner, provided that the resulting composite is substantially free from amorphous silica. Thus, the crystalline aluminosilicate and alumina may be dry mixed as finely divided particles in the 50—150 micron range and the mixture combined with a binder or lubricant such as starch, polyvinyl alcohol, methylcellulose, graphite, etc., and compressed into pills, extrudates, or the like as is commonly practiced. An alternative method is to homogenize the crystalline aluminosilicate and alumina in sufficient water to form a slurry in the nature of a colloidal suspension comprising from 10 to 40 wt. % solids, the slurry being sprayed in an atomized state into a tower of hot inert gases whereby a rapid evaporation of water occurs and dried particles of a predetermined size range fall out of the spray. The spray-dried particles are then compressed into pills, pellets, extrudates, etc., as aforesaid. In any case, the crystalline aluminosilicate is suitably composited with the alumina in a weight ratio of from 2:1 to 9:1.

Although naturally-occurring alumina, such as is recovered from bauxite, may be employed as a component of the crystalline aluminosilicate-alumina composite, the alumina is preferably a synthetically-prepared alumina. In the present specification, alumina is intended as porous aluminum oxide in its various states of hydration. One preferred type of alumina is gamma-alumina, the preparation of which is well known. For example, gamma-alumina may be prepared by calcining an alumina hydrogel such as is commonly formed by adding a precipitating agent, such as ammonium hydroxide, to an aluminum salt solution, such as an aqueous aluminum chloride solution. Synthetic gamma-aluminas may also be prepared by the reaction of hydrochloric acid with an excess of aluminum, the resulting hydrosol being subsequently gelled by the addition of a precipitating agent, for example ammonium hydroxide, and the resulting gel dried and calcined at a sufficient temperature to convert the same to gamma-alumina. An alpha-alumina monohydrate of the boehmite structure, such as is recovered as a by-product in the manufacture of alcohol through hydrolysis of an aluminum alcoholate or alkoxide, may also be employed. In any case, the alumina may be activated by one or more treatments including drying, calcining, steaming, or treatment with various chemical agents to develop a highly porous material.

The crystalline aluminosilicates employed herein are well known in the art. Such materials are of an ordered crystalline structure comprising cages or cavities interconnected by smaller pores or channels of a definite size range characteristic of each crystalline aluminosilicate variety. Since the

dimensions of the pores and channels are such as to accept molecules of certain dimension while rejecting those of larger dimension the materials have come to be known as molecular sieves and utilized in many ways taking advantage of these properties.

The crystalline aluminosilicates are generally described as a three-dimensional network of fundamental structural units consisting of silicon-centered  $\text{SiO}_4$  and aluminum-centered  $\text{AlO}_4$  tetrahedra interconnected by a mutual sharing of apical oxygen atoms. To effect a chemical balance, each  $\text{AlO}_4$  tetrahedra has a cation associated therewith, typically sodium. In most cases, substantially all of the sodium cations are subsequently exchanged with hydrogen cations to yield the hydrogen or active form of the crystalline aluminosilicate.

The  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra are arranged in a definite geometric pattern often visualized either in terms of chains, layers or polyhedra. In any case, the crystalline aluminosilicates comprise well-defined intracrystalline dimensions including intracrystalline channels and pores whose narrowest cross-section has essentially a uniform diameter. The various crystalline aluminosilicates may be classified according to the geometric pattern of their framework with its attendant pore size, and by the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio of their composition.

Preferably, the crystalline aluminosilicate is a synthetically-prepared X or Y type crystalline aluminosilicate, or a naturally-occurring faujasite. The preferred materials are characterized by basically similar crystal-lattice structures. Thus, the aforementioned fundamental structural units,  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra are joined to form four-membered and six-membered rings and the rings so arranged that the resulting structure resembles a truncated octahedron with the four-membered ring forming six sides or faces thereof and the six-membered ring forming the remaining eight sides or faces. The resulting truncated octahedra are interconnected at the hexagonal faces through a hexagonal prism formed by two of the six-membered rings of tetrahedra to form a crystal lattice comprising cavities or cages in open communication through channels permitting three-directional access thereto. In general, the preferred crystalline aluminosilicates are characterized by a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of from 2 to 6 and by pore openings in the range of from 6 to 15 Angstroms, the synthetically prepared X type having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of from 2 to 3, and the Y type having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in excess of 3. The preferred crystalline aluminosilicates may be prepared according to well-known methods such as are set out in U.S.

Patent No. 2,882,244 and U.S. Patent No. 3,130,007.

Typically, in the manufacture of crystalline aluminosilicates an excess of amorphous silica is utilized as a reactant and the product invariably contains a substantial amount of residual amorphous silica. However, in accordance with the present invention, the composite of crystalline aluminosilicate and alumina is utilized substantially free from amorphous silica and contains less than 4 wt. % alkali metal. One convenient and preferred method of reducing both the amorphous and the alkali metal content to acceptable levels comprises treating the crystalline aluminosilicate one or more times in contact with an aqueous solution containing ammonium cations, suitably an aqueous solution of an ammonium salt such as ammonium sulfate.

In the course of reducing the amorphous silica content of the crystalline aluminosilicate in the described manner, substantially all of the alkali metal cations associated with the crystalline aluminosilicate are base-exchanged with ammonium cations, the crystalline aluminosilicate being subsequently dried and heat treated to form the hydrogen or active form thereof. The crystalline aluminosilicate of this invention is preferably, a magnesium-exchanged crystalline aluminosilicate, the crystalline aluminosilicate containing sufficient magnesium cations to yield a final catalyst composite containing from 0.2 to 1.5 wt. % magnesium. Base exchange of the crystalline aluminosilicate to introduce magnesium cations may be accomplished prior to drying the last mentioned ammonia-exchange crystalline aluminosilicate by contacting the same with an aqueous magnesium salt solution, suitably from a 1 to a 5% aqueous magnesium chloride solution, one or more times at conventional ion-exchange conditions including a pH of from 4 to 7. Base exchange of the crystalline aluminosilicate to exchange a given portion of the ammonium cations for magnesium cations can be effected before or after the alumina component has been composited with the crystalline aluminosilicate. In any case, the crystalline aluminosilicate is subsequently dried and heat treated to decompose ammonium cations and form the active or hydrogen form of the crystalline aluminosilicate.

The hydrogenation component supported on the described crystalline aluminosilicate-alumina composite contains as a major portion thereof a catalytic constituent comprising a Group VIII metal component, and as a minor portion a promoter comprising a Group VIB metal component. Thus, the hydrogenation component will comprise molybdenum, chromium and/or tungsten components as promoter together with one

or more Group VIII metal components, i.e., components of one or more metals selected from iron, nickel, cobalt, platinum, palladium, ruthenium, rhodium, osmium, and iridium, as catalyst constituent. The hydrogenation component, including the catalytic constituent and promoter, will suitably comprise from 5 to 15 wt. % of the final catalyst composition. In any case the hydrogenation component itself comprises from 60 to 90 wt. % catalytic constituent i.e. Group VIII metal component (calculated as metal), with the promoter i.e. Group VIB metal component comprising from 10 to 40 wt. % thereof (calculated as metal), in other words the catalytic constituent and promoter are present in a weight ratio of from 1.5:1 to 9:1 (calculated as the metals). While the promoter does not necessarily effect an improvement in activity or selectivity of the catalyst composition in a hydrocracking operation, its use as a minor portion of the hydrogenation component as herein contemplated is a major factor contributing to the unusual stability exhibited by the catalyst composition of this invention. In one preferred embodiment of this invention, the hydrogenation component will comprise from 60 to 80 wt. % Group VIII metal component, e.g. nickel, and from 20 to 40 wt. % Group VIB metal component, e.g. molybdenum, (calculated as metals), i.e. a weight ratio of 1.5:1 to 4:1 (calculated as the metals).

The hydrogenation component may be supported on the crystalline aluminosilicate-alumina composite by any convenient means. One method comprises impregnating a soluble compound of a selected metallic component on the crystalline aluminosilicate-alumina composite from an aqueous solution thereof. The soluble compound serves as a precursor of the desired metallic component such that, upon subsequent heating at conditions effecting decomposition of said compound, the desired metallic component is formed supported on the crystalline aluminosilicate-alumina composite. Soluble Group VIB metal compounds which may be employed include ammonium molybdate, ammonium paramolybdate, molybdic acid, ammonium chromate, ammonium peroxychromate, chromium acetate, chromous chloride, chromium nitrate, ammonium metatungstate, tungstic acid, etc. The Group VIB metal compound and the Group VIII metal compound are conveniently impregnated on the crystalline aluminosilicate-alumina composite utilizing a common aqueous impregnating solution thereof. Suitable Group VIII metal compounds include nickel nitrate, nickel sulfate, nickel chloride, nickel bromide, nickel fluoride, nickel iodide, nickel acetate, nickel formate, cobaltous nitrate, cobaltous sulfate, cobaltous

fluoride, ferric fluoride, ferric bromide, ferric nitrate, ferric sulfate, ferric formate, ferric acetate, platinum fluoride, chloroplatinic acid, chloropalladic acid, palladium fluoride, etc.

Impregnation can be accomplished by conventional techniques whereby the crystalline aluminosilicate-alumina composite is soaked, dipped, suspended or otherwise immersed in the impregnating solution at conditions to absorb a soluble compound of a selected metallic component. Certain impregnating techniques are preferred. Thus, impregnation of the Group VIB and Group VIII metal components is preferably from a common aqueous ammoniacal solution of soluble compounds thereof, for example, an ammoniacal solution of molybdic acid and nickel nitrate. Further, the impregnation is preferably effected utilizing a minimal volume of impregnating solution commensurate with an even distribution of the hydrogenation components on the crystalline aluminosilicate-alumina composite. One preferred method involves the use of a steam jacketed rotary dryer. The crystalline aluminosilicate-alumina composite is immersed in the impregnating solution contained in the dryer and tumbled therein by the rotating motion of the dryer, the volume of the crystalline aluminosilicate-alumina composite so treated being initially in the range of from about 0.6 to 1.0 with respect to the volume of the impregnating solution. Evaporation of this solution in contact with the crystalline aluminosilicate-alumina composite is expedited by applying steam to the dryer jacket. The evaporation is further facilitated by a continuous purge of the dryer utilizing a flow of dry gas, suitably air or nitrogen. In any case, the impregnating solution is normally evaporated at conditions to reduce the volatile matter of the impregnated composite to less than 30 wt. % as determined by weight loss on ignition at 900°C.

The dried composite is normally subsequently calcined in an oxidizing atmosphere at a temperature of from 600° to 1200°F. over a period of from 1 to 6 hours. Preferably, the dried composite is calcined in a stream of air at a temperature of from 600° to 925°C., and more preferably in a stream of air at a temperature of from 600° to 650°F. for a period of at least 1 hour, and thereafter at a temperature of from 875 to 925°F. for a period of at least 2 hours.

The following examples are presented in illustration of the catalyst composition of this invention.

#### EXAMPLE I

$\frac{1}{3}$ " faujasite-alumina particles, having a surface area of about 550 m<sup>2</sup>/gm and an

average bulk density of about 0.575 gms/cc, were impregnated with 5.2 wt. % nickel and 2.3 wt. % molybdenum. The particles consisted of 75% ammonium and magnesium-exchange type Y faujasite and 25 wt. % alumina. The faujasite-alumina particles contained about 0.7 wt. % magnesium and less than 1.3 wt. % sodium and were substantially free from amorphous silica. The nickel and molybdenum components were impregnated on the faujasite-alumina particles from a common impregnating solution prepared by dissolving 27 pounds of 85% molybdic acid and 173.5 pounds of nickel nitrate hexahydrate in 80 gallons of 12 wt. % aqueous ammonia solution. The impregnating solution was subsequently diluted to 100 gallons with the aqueous ammonia solution and added to 600 pounds of the faujasite-alumina particles in a steam-jacketed rotary evaporator. The evaporator was rotated for about 15 minutes after which steam was applied to the jacket and the impregnating solution evaporated in contact with the particles. The particles were dried in the evaporator until they exhibited less than 30 wt. % loss on ignition at 900°C. The dried particles were thereafter heated in a stream of air, first at 625°F. for one hour, and then at 900°F. for two hours. The finished catalyst composition had a surface area of about 450 m<sup>2</sup>/gm and an average bulk density of 0.64 gms/cc. The catalyst composition is hereinafter referred to as Catalyst I.

#### EXAMPLE II

To provide a measure of comparison, a catalyst was prepared substantially as described in Example I except that a palladium component was substituted for the nickel and molybdenum components, the palladium being incorporated in the magnesium-exchanged faujasite-alumina particles by ion-exchange with an aqueous chloropalladic acid solution at 180°F. for about 1 hour to yield a catalyst composition comprising 0.53 wt. % palladium. The catalyst is hereinafter referred to as Catalyst II.

Catalysts I and II were presulfided and evaluated with respect to the hydrocracking of a pretreated 400°F. + Farmer's Union vacuum gas oil fraction. The hydrocarbon charge, including unconverted recycle material, was processed over each of the catalysts (400 cc.) in admixture with 10,000 standard cubic feet of hydrogen per barrel of charge stock at a liquid hourly space velocity of 0.6 and at a pressure of 2000 psig. The peak reactor temperature was adjusted to effect a 50 liquid volume % conversion of the vacuum gas oil to a 400°F. end point gasoline fraction, and the temperature was periodically adjusted upwardly as required to maintain said conver-

sion.  $C_4$  product was stripped from the reactor effluent and the effluent treated in a fractionator for the separation and recovery of  $C_5$  + product and recycle of unconverted material to achieve an ultimate conversion of 100 liquid volume %.

At a catalyst life of 1.0 barrel of charge per pound of catalyst, Catalyst I required 738.5°F. peak reactor temperature to maintain a 50 liquid volume % conversion. The  $C_4$  yield was 17.6 liquid volume %, and the  $C_3$  + yield 108.7 liquid volume %. Catalyst I had a relatively high activity at this stage as indicated by a peak reactor temperature of 720.5°F., with relatively low  $C_4$  yields (14.5 liquid volume %) and good  $C_3$  + yields (112 liquid volume %). However, catalyst stability in the latter case was relatively poor and catalyst life was relatively short. The improved stability of Catalyst I relative to Catalyst II is apparent with reference to the attached drawing wherein catalyst life is plotted against reactor temperature (Figure 1),  $C_4$  yield (Figure 2) and  $C_3$  + yield (Figure 3) over the life of the catalyst ranging from 5.0 to 8.5 barrels of charge per pound of catalyst.

#### WHAT WE CLAIM IS:—

1. A catalyst composition comprising a hydrogenation component supported on a crystalline aluminosilicate composited with alumina, the composite being substantially free from amorphous silica and containing less than 4 wt. % alkali metal and the hydrogenation component comprising a Group VIII metal component and Group VIB metal component in a weight ratio (calculated as metals) of from 1.5:1 to 9:1.
2. A catalyst composition as claimed in claim 1 wherein the crystalline aluminosilicate is a magnesium-exchanged crystalline aluminosilicate.
3. A catalyst composition as claimed in claim 2 wherein the crystalline aluminosilicate has been base-exchanged with magnesium ions to the extent that the composite contains from 0.2 to 1.5 wt. % magnesium.
4. A catalyst composition as claimed in claim 2 or 3 wherein the crystalline aluminosilicate is a magnesium-exchanged type Y crystalline aluminosilicate.
5. A catalyst composition as claimed in any one of claims 1 to 4 wherein the crystal-

line aluminosilicate is composited with alumina in a weight ratio of from 2:1 to 9:1.

6. A catalyst composition as claimed in any of claims 1 to 5 wherein the hydrogenation component constitutes from 5 to 15 wt. % of said catalyst composition.

7. A catalyst composition as claimed in any of claims 1 to 6 wherein the Group VIII metal component is a nickel component and the Group VIB metal component is a molybdenum component.

8. A catalyst composition as claimed in any of claims 1 to 7 wherein the Group VIII metal component and the Group VIB metal component are present in a weight ratio (calculated as metals) of from 1.5:1 to 4:1.

9. A catalyst composition as claimed in any of claims 1 to 8 wherein the alumina is gamma-alumina and the crystalline aluminosilicate is a type X or type Y synthetically prepared material or a naturally occurring faujasite.

10. A catalyst composition as claimed in any of claims 1 to 9 wherein the crystalline aluminosilicate in the composite has been treated one or more times in contact with an aqueous solution of an ammonium salt to remove amorphous silica and to reduce the alkali metal content below 4 wt. %.

11. A catalyst composition as claimed in any of claims 1 to 10 which has been prepared by impregnating the composite with the hydrogenation component, drying the impregnated composite and calcining it in an oxidizing atmosphere at a temperature of from 600 to 1200°F. for from 1 to 6 hours.

12. A catalyst composition as claimed in claim 1 and substantially as described in the foregoing Example 1.

13. A process for catalytic hydrocracking of a petroleum or heavy petroleum fraction in which a catalyst composition as claimed in any of claims 1 to 12 is employed as the catalyst.

14. A process as claimed in claim 13 wherein the catalyst is presulfided prior to use.

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FIG. 1

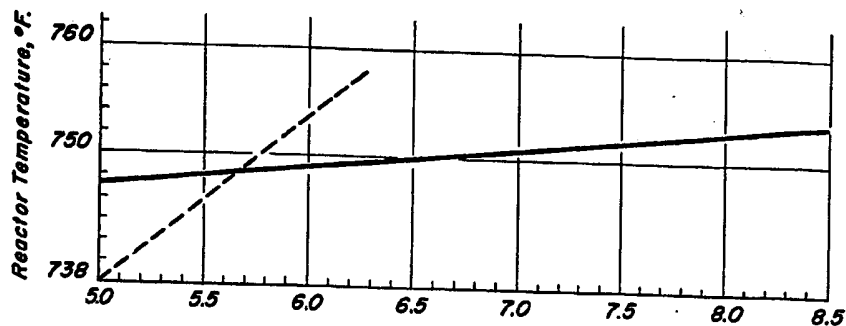


FIG. 2

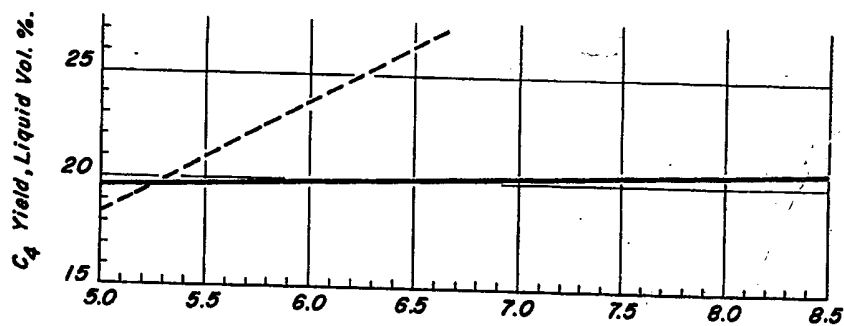
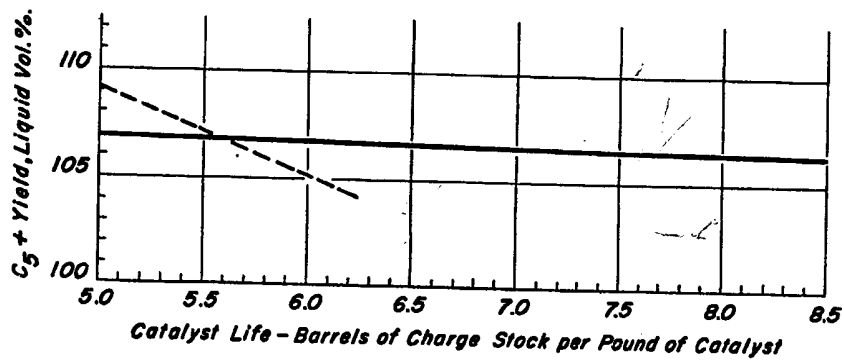


FIG. 3



— Catalyst I  
--- Catalyst II